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(54) Title: FLUOROPOLYMER-EPOXY RESIN SEMI-INTERPENETRATING NETWORK COMPOSITION		
(57) Abstract A curable composition comprising a curable epoxy resin, an effective amount of a curative for the curable epoxy resin, a fully prepolymerized uncrosslinked fluoropolymer, and optionally a polyolefin or a polyamide. Up to 20 weight percent of the fluoropolymer can be dehydrofluorinated to provide a semi-IPN having increased adhesion to substrates. The fluoropolymer-epoxy semi-IPNs are useful as protective coatings, adhesives including adhesive tapes and in multilayer assemblies.		

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FLUOROPOLYMER-EPOXY RESIN SEMI-INTERPENETRATING NETWORK COMPOSITION**5 Field of the Invention**

This invention relates to semi-interpenetrating polymer networks (semi-IPNs) of thermoplastic resins and thermosetting resins prepared by polymerization of a thermosetting resin (i.e., an epoxy resin) in the presence of a fully prepolymerized thermoplastic fluoropolymer. The invention also provides a method
10 of preparing semi-IPNs that feature 100% solids processing and latent- or post-curing of the epoxy resin, and uses for the semi-IPNs produced by the method.

Background of the Invention

Blending a small amount of elastomeric or thermoplastic material into a
15 hardenable thermosetting resin in order to toughen (i.e., increase the ductility of) the thermoset is a common practice in industry. Elastomeric or thermoplastic toughening agents include natural rubbers, polyolefins, and vinyl copolymers such as poly(styrene-co-butadiene). In such cases, the toughening agent is blended in a ratio of from about 1:20 to about 1:4 with a curable thermosetting resin such that
20 the thermoplastic component becomes the dispersed phase in a thermosetting resin providing the continuous phase. See, for example, U.S. Patent Nos. 4,861,647 and 5,008,135.

Solvent-based blends of fluoropolymers and thermosetting resins have been described in U.S. Patent Nos. 3,784,506 and 4,179,542 as useful for coatings on
25 metal substrates for corrosion protection. These coatings are prepared by ball milling or high-shear mixing of solid resins and a dispersing solvent, followed by application of the dispersion to the metal substrate, typically by spray coating, followed by baking at temperatures up to 250° C. Coating of a 100% solids semi-IPN is not described.

30 The photoinitiated cationic polymerization of epoxides is known. Organic aryl sulfonium and aryl iodonium salts are recognized as suitable photoinitiators, i.e., compounds which, after irradiation with light, release protons which initiate,

e.g., epoxide polymerization. Also, certain complex metal-arene organometallic salts have been described as photoinitiators for cationic polymerizations. In these cases, the cationically polymerizable components are monomers.

5 Summary of the Invention

Briefly, this invention provides a curable composition comprising:

- a) a curable epoxy resin,
- b) an effective amount of a curative for the curable epoxy resin,
- c) a fully prepolymerized uncrosslinked fluoropolymer, and
- 10 d) optionally, a polyolefin or a polyamide,

wherein said composition is free of solvent.

Preferably, the epoxy component is present in a range of more than zero and up to 75 weight percent, more preferably more than zero up to 70 weight percent, even more preferably more than zero up to 40 weight percent, and most preferably
15 0.5 to 15 weight percent, and the fluoropolymer is present in a range of 25 to less than 100 weight percent, more preferably 30 to less than 100 weight percent, even more preferably 60 to less than 100 weight percent, and most preferably 85 to 95.5 weight percent, based on the total composition. The composition preferably is free of curatives which physically integrate fluorine into the backbone of the cured
20 epoxy.

In another aspect, the present invention describes a semi-interpenetrating polymer network comprising a thermally and/or photochemically cured epoxy resin and a fully pre-polymerized fluoropolymer.

In another aspect, the present invention describes a method of preparing a
25 semi-IPN comprising the steps of (a) in the absence of a solvent, intimately mixing a fully prepolymerized fluoropolymer optionally in combination with one or both of a polyolefin and a polyamide, both of which preferably are uncrosslinked, in the presence of a photochemically- or thermally-curable epoxy resin, and at least one photo curing agent or high-temperature stable thermal curing agent for the epoxy
30 resin, (b) optionally, applying the solvent-free mixture to a substrate, and (c) at

any subsequent time after mixing, activating the curing agent or photocatalyst by supplying sufficient thermal and/or photo energy to the mixture.

In a further aspect, dehydrofluorination of the fluoropolymer prior to combining with an epoxy monomer, optionally in the presence of a polyolefin or a polyamide, provides a semi-IPN having increased adhesion to a substrate.

What has not been described in the art, and is provided by the present invention, is a solvent-free curable composition comprising a curable thermosetting resin, i.e., an epoxy resin and a curative therefor, and a fully pre-polymerized fluoroelastomer, optionally in the presence of a polyolefin or polyamide, wherein the curable epoxy resin preferably is not exposed to curing conditions, i.e., irradiation by light, preferably UV light, or temperatures greater than about 170° C, in the presence of a suitable onium salt photoinitiator such as Ar_3SSbF_6 (wherein "Ar" refers to an aromatic species such as, for instance, phenyl), or a fluorene amine as curing agent until the composition is formed in place, molded, coated, or otherwise prepared in a useful format. Other curing agents permit processing at higher temperatures.

The fluoropolymer-epoxy semi-IPNs are useful as protective coatings, adhesives, and in multilayer assemblies. More particularly, the semi-IPNs of the invention are useful as structural adhesives for metals, plastics, glass or ceramics; as free-standing hot melt adhesives, or as a protective coatings. In a preferred embodiment, the fluoropolymer-epoxy semi-IPN can be coated on a flexible substrate to produce an adhesive tape. In an additional preferred embodiment, the fluoropolymer-epoxy semi-IPN can be coated on a polymeric tank or vessel, preferably comprising a polyolefin, more preferably comprising polypropylene, used for storage or transporting hydrocarbon fuels such as gasoline, wherein the semi-IPN of the invention can be an intermediate (or "tie") coating that acts as a binding agent between the polymeric vessel and a subsequent fluoropolymer (e.g., poly(tetrafluoroethylene) (PTFE)) protective coating. Semi-IPNs of the invention also find use directly as interior coatings for metal tanks or vessels used for transportation and storage of corrosive chemicals.

In this application:

"epoxy resin" means a hardenable material and includes mono- and polyepoxides;

"backbone" means the main polymer chain and not including pendent or end groups;

5 "cationic organometallic salt" means a salt, the cationic portion of which contains at least one carbon atom of an organic group bonded to a metal atom ("Basic Inorganic Chemistry", F. A. Cotton, G. Wilkinson, Wiley, New York, 1976, p 497); preferably the metal atom is a transition metal atom;

10 "group" means a chemical species that allows for substitution or which may be substituted by conventional substituents which do not interfere with the desired product, e.g., substituents can be alkoxy, phenyl, halo (F, Cl, Br, I), cyano, nitro, etc.;

"semi-interpenetrating polymer network (semi-IPN)" means a polymer network of two or more polymers wherein at least one polymer is crosslinked and at 15 least one polymer is uncrosslinked,

"fluoroelastomer" means a fluorinated polymer having properties of natural or synthetic rubber in that it stretches under tension, has a high tensile strength, retracts rapidly, and recovers its original dimensions fully, and can also exhibit plasticity such that when deformed to the limit, it fails;

20 "fluoropolymer" or "fluorocarbon polymer" means a polymer prepared from at least one monomer in which at least half of the hydrogen atoms directly attached to carbon atoms have been replaced by fluorine atoms;

"dehydrofluorination" means removal of HF from a fluorocarbon unit of a polymer to produce an unsaturated unit in the polymer; and

25 "curative," "curing agent," "catalyst," and "initiator" are used interchangeably to mean any active or reactive species used to effect a polymerization reaction.

Semi-IPNs of the present invention have advantageous properties in that the fluoropolymer component can contribute to electrical properties, chemical 30 resistance, and low usage temperature, and the epoxy monomer component

contributes to stability, formulation flexibility, and post-curability of the composition.

Detailed Description of the Preferred Embodiments

- 5 The present invention provides a curable composition comprising:
- a) a curable epoxy resin,
 - b) an effective amount of a curative for the curable epoxy resin, and
 - c) a fully prepolymerized uncrosslinked fluoropolymer, and optionally a polyolefin or polyamide.

- 10 Preferably, blending of the components takes place at a temperature that is below the thermal activation temperature of the catalyst, i.e. 170° C or higher, preferably in the range of 170 to 400° C, more preferably in the range of 200 to 400° C.

- Useful fluoropolymers can be prepared by methods known in the art and are
- 15 also commercially available, for example from Dyneon LLC, St. Paul, MN, under the trade names THV™ 200, THV 230, THV 500, THV 530, Fluorel™ (HFP/VDF), Fluorel-11™ (TFE/PP/VDF), and Kel-F™ 800, fluoroelastomer; from Elf Atochem North America Inc. (Philadelphia, PA), under the trade names Kynar™ 740, 2800, 9301; from Kureha Chemical Co. under the trade name KF™
- 20 polymer; From Daikin America, Inc.(New York, NY), under the trade name Neofluron™ VDF; from Central Glass (Tokyo, Japan) under the trade name Cefral Soft™ G-150, and from Asahi Glass Co., Ltd.(Tokyo, Japan), under the trade name AFLAST™ 200.

- In a more preferred embodiment, the fully polymerized fluoropolymer is a
- 25 terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride (hereinafter designated THV, available from Dyneon LLC, St. Paul, MN). Most preferably, THV 200 (42 mole percent TFE, 20 mole percent HFP, 30 mole percent VDF) is used. The terpolymer backbone comprises units arising from the following monomers:

	<u>source</u>	<u>unit</u>
5	tetrafluoroethylene (TFE)	$ \begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{F} \end{array} $
10	hexafluoropropylene (HFP)	$ \begin{array}{cc} \text{F} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{F} & \text{CF}_3 \end{array} $
15	vinylidene fluoride (VDF)	$ \begin{array}{cc} \text{H} & \text{F} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{F} \end{array} $
20		

In addition to THV and others mentioned above, fluoropolymers that can be useful in the present invention include in general, homopolymers and copolymers prepared from the group comprising tetrafluoroethylene, chlorotrifluoroethylene, hexafluoropropene, vinylidene fluoride, perfluoroalkyl vinyl ethers such as perfluoropropyl vinyl ether, and trifluoroethylene. Specific polymers include, but are not limited to, poly(ethylene-co-chlorotrifluoroethylene) (ECTFE), poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(ethylene-co-tetrafluoroethylene) (ETFE), poly(ethylene-co-tetrafluoroethylene-co-hexafluoropropylene) (EFEP), poly(vinylidene fluoride) (PVDF), and poly(chlorotrifluoroethylene) (PCTFE). Of course, many other fluoropolymers are known in the art that can be useful in the invention.

In a further aspect, dehydrofluorination of the fluoropolymer prior to combining with an epoxy monomer, and optionally a polyolefin or polyamide, provides a semi-IPN having increased adhesion to a substrate. Dehydrofluorination of a fluoropolymer incorporated in a semi-IPN of the invention can provide desirable adhesive properties toward substrates. The mole percent of dehydrofluorination present in the fluoropolymer can be in the range of 0.01 to 20,

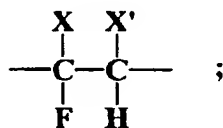
preferably 0.01 to 5.0, more preferably 0.02 to 2.0 mole percent, more preferably 0.2 to 1.15 mole percent.

The fluoropolymer can be dehydrofluorinated by any method that will provide sufficient carbon-carbon unsaturation of the fluoropolymer to create
5 increased bond strength between the fluoropolymer and a substrate. Preferably, the dehydrofluorination process will not introduce into the fluoropolymer a significant amount of grafted substituents. By "a significant amount," it is meant, for instance, an amount greater than about 2 mole percent, based on the number of
10 interpolymerized monomeric units comprising the dehydrofluorinated fluoropolymer. Desirably, fewer than about 1 mole percent adhesion-promoting groups are grafted onto the fluorinated polymer during dehydrofluorination, e.g., fewer than about 0.5, preferably 0.2, or most preferably 0.1 mole percent, based on
the total number of interpolymerized polymeric units comprising the dehydrofluorinated fluoropolymer. In the case of dehydrofluorinated bulk
15 fluoropolymer, the introduction of less than a significant amount of grafted substituents onto the fluoropolymer will preferably not alter by a measurable amount the physical or mechanical properties of the fluoropolymer.

Many suitable dehydrofluorination methods are known in the fluoropolymer art. For example, dehydrofluorination of bulk fluoropolymer can be accomplished
20 by solvent-based methods wherein a fluoropolymer is dissolved in a solution of organic solvent. A basic reagent is added to the solution to cause dehydrofluorination, optionally in the presence of a phase transfer catalyst. Typical solvents include tetrahydrofuran, methyl isobutyl ketone, methyl ethyl ketone, acetone, n,n-dimethyl formamide, dimethylacetamide, etc. See, for example, U.S.
25 Patent Nos. 3,507,844, 4,742,126, and 4,758,618. Alternatively dehydrofluorination can be accomplished in a two phase solvent method wherein fluoropolymer is dissolved in an organic solvent, and this solvent phase is mixed with an aqueous phase containing an alkali metal hydroxide and a phase transfer catalyst. Useful catalysts are known in the fluoropolymer art and include, for
30 example, tetrabutylammonium bromide (TBAB), tetraalkyl phosphonium halides, alkylarylphosphonium halides, alkyl ammonium halides, and alkyl phosphonium

halides. See U.S. Patent No. 4,742,126. According to yet another method, fluoropolymers can be dehydrofluorinated by dry, bulk dehydrofluorination methods referred to in the art as "reactive extrusion methods." By these methods, dehydrofluorination is achieved by a dry basic process using, e.g., an extruder or a bowl mixer.

Dehydrofluorination of fluoropolymer within an aqueous fluoropolymer emulsion can be also accomplished under relatively mild conditions in a basic, aqueous medium containing substantially no organic solvent, preferably in a 100 percent aqueous medium that contains no organic solvent, and optionally in the presence of a suitable emulsifying surfactant. By this aqueous dehydrofluorination method, a basic compound can be added to a fluoropolymer emulsion that contains a fluoropolymer having a structural segment according to formula (1):



(1)

wherein X and X' are each independently either hydrogen or an electron-withdrawing group. The hydrogen atom is sufficiently acidic to result in dehydrofluorination of the fluoropolymer upon the addition of a base compound to the fluoropolymer emulsion.

Examples of suitable basic compounds include ethylamine, hydroxides such as potassium hydroxide (KOH), ammonium hydroxide (NH₄OH), sodium hydroxide (NaOH), lithium hydroxide (LiOH); carbonates such as potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), etc.

The basic compound is added to the emulsion in an amount that does not disrupt the stability of the emulsion, and therefore does not cause coagulation of the fluoropolymer. As used within the present description, the term "coagulation" refers to the condition of fluoropolymer precipitation out of the emulsion. Then, the emulsion can be subjected to reaction conditions sufficient to allow the basic compound to react across the -CFX-CHX' reaction site of the fluoropolymer, and to thereby remove a hydrogen and a fluorine atom from the fluoropolymer to

produce an unsaturated $-CX=CX'$ - sequence within the fluoropolymer. The aqueous dehydrofluorination reaction conditions (i.e., reaction time and temperature) can be any reaction time and any reaction temperature that allow the dehydrofluorination reaction to occur, and can depend on the particular fluoropolymer and base compounds chosen, as well as the desired degree of unsaturation of the resulting dehydrofluorinated fluoropolymer. In this aqueous dehydrofluorination method, the reaction temperature can be relatively mild, for instance in the range from about 40 to 100 degrees Celsius. The reaction time can be any useful reaction time, but can preferably be in the range from about 6 to 100 hours.

The emulsifying surfactant within the fluoropolymer emulsion can be one of various emulsifying surfactant known in the fluoropolymer emulsion art. These include, for example, anionic surfactants such as fatty acid soaps (sodium or potassium stearate, laurate, palmitate), sulfates and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate), nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose, and fluorinated surfactants including perfluorinated carboxylic acids. These and other emulsifying surfactants can be used alone or in combinations of two or more emulsifying surfactants, and can be present in any effective amount, i.e., an amount that will result in an emulsion. (See, e.g., George Odian, *Principles of Polymerization*, 3332-3 (2nd ed., 1981.))

The above-described dehydrofluorination methods relate to the dehydrofluorination of bulk fluoropolymer (e.g., fluoropolymer granules), or fluoropolymer emulsions. In these bulk and emulsion-type dehydrofluorination processes, the amount of dehydrofluorination of the fluoropolymer can preferably be in the range from about 0.01 mole percent to 20 mole percent, based on the number of interpolymerized monomeric units used to prepare the dehydrofluorinated fluoropolymer, with the range from about 0.02 mole percent to about 2.0 mole percent being particularly preferred.

Two embodiments using a dehydrofluorinated polymer include the following:

1. Cure of an epoxy monomer in the presence of a dehydrofluorinated polymer provides a semi-IPN with some chemical binding between the epoxy and fluoropolymer chains.

2. Cure of an epoxy in the presence of a blend of dehydrofluorinated polymer and functionalized (*i.e.*, acidified, *e.g.*, maleated) polyolefin provides a semi-IPN with some chemical binding between the epoxy and fluoropolymer chains and between epoxy and polyolefin chains.

Epoxy resins useful in the invention preferably comprise compounds which comprise one or more 1,2-, 1,3- and 1,4-cyclic ethers, which also may be known as 1,2-, 1,3- and 1,4-epoxides. The 1,2-cyclic ethers are preferred. Such compounds can be saturated or unsaturated, aliphatic, alicyclic, aromatic or heterocyclic, or can comprise combinations thereof. Compounds that contain more than one epoxy group (*i.e.*, polyepoxides) are preferred. Monoepoxy monomers useful in the present invention include 3-hydroxy-1,2-propylene oxide, oxacyclobutane, cyclohexene oxide, indene oxide, styrene oxide, butyl glycidyl ether, phenyl glycidyl ether, cresyl glycidyl ether, n-butylphenol glycidyl ether, vinylcyclohexane monoxide, octylene oxide, alpha-pinene oxide, limonene oxide, and 3-pentadecylphenyl glycidyl ether.

Aromatic polyepoxides (*i.e.*, compounds containing at least one aromatic ring structure, *e.g.*, a benzene ring, and more than one epoxy group) that can be used in the present invention include the polyglycidyl ethers of polyhydric phenols, such as Bisphenol A-type resins and their derivatives, epoxy cresol-novolac resins, Bisphenol-F resins and their derivatives, and epoxy phenol-novolac resins; and glycidyl esters of aromatic carboxylic acids, *e.g.*, phthalic acid diglycidyl ester, isophthalic acid diglycidyl ester, trimellitic anhydride triglycidyl ester, and pyromellitic acid tetraglycidyl ester, and mixtures thereof. Preferred aromatic polyepoxides are the polyglycidyl ethers of polyhydric phenols, such as the EPON™ series of diglycidyl ethers of Bisphenol-A, including EPON 828 and EPON 1001F, available commercially from Shell Chemicals, Inc., Houston, TX.

Representative aliphatic cyclic polyepoxides (*i.e.*, cyclic compounds containing one or more saturated carbocyclic rings and more than one epoxy group,

also known as alicyclic compounds) useful in the present invention include the "ERL™" series of alicyclic epoxides commercially available from Union Carbide Corp., Danbury, CT, such as vinyl cyclohexene dioxide (ERL-4206), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (ERL-4221), 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate (ERL-4201), bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate (ERL-4289), dipentene dioxide (ERL-4269), as well as 2-(3,4-epoxycyclohexyl-5,1''-spiro-3'',4''-epoxycyclohexane-1,3-dioxane, 4-(1,2-epoxyethyl)-1,2-epoxycyclohexane and 2,2-bis(3,4-epoxycyclohexyl)propane. Preferred alicyclic polyepoxides are the ERL™ series.

Representative aliphatic polyepoxides (*i.e.*, compounds containing no carbocyclic rings and more than one epoxy group) include 1,4-bis(2,3-epoxypropoxy)butane, polyglycidyl ethers of aliphatic polyols such as glycerol, polypropylene glycol, 1,4-butanediol, and the like, and the diglycidyl ester of linoleic dimer acid.

A wide variety of commercial epoxy resins are available and are listed or described in, *e.g.*, the *Handbook of Epoxy Resins*, by Lee and Neville, McGraw-Hill Book Co., New York (1967), *Epoxy Resins, Chemistry and Technology*, Second Edition, C. May, ed., Marcell Dekker, Inc., New York (1988), and *Epoxy Resin Technology*, P. F. Bruins, ed., Interscience Publishers, New York, (1968). Any of the epoxy resins described therein may be useful in preparation of the semi-IPNs of the invention.

Optionally, monohydroxy- and polyhydroxy-alcohols may be added to the curable compositions of the invention, as chain-extenders for the epoxy resin. Suitable examples of alcohols include but are not limited to methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, pentaerythritol, 1,2-propanediol, ethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexane dimethanol, 1,4-cyclohexanediol and glycerol. Preferably, compounds containing hydroxyl groups, particularly compounds containing from about 2 to 50 hydroxyl groups and above all, compounds having a weight average molecular weight of from about 50 to 25,000, preferably from about

50 to 2,000, for example, polyesters, polyethers, polythioethers, polyacetals, polycarbonates, poly(meth)acrylates, and polyester amides, containing at least 2, generally from about 2 to 8, but preferably from about 2 to 4 hydroxyl groups, or even hydroxyl-containing prepolymers of these compounds, are representatives
5 compounds useful in accordance with the present invention and are described, for example, in Saunders, *High Polymers, Vol. XVI*, "Polyurethanes, Chemistry and Technology," Vol. I, pages 32-42, 44-54 and Vol. II, pages 5-6, 198-99 (1962, 1964), and in *Kunststoff-Handbuch*, Vol. VII, pages 45-71 (1966). It is, of course, permissible to use mixtures of the above-mentioned compounds containing at least
10 two hydroxyl groups and having a molecular weight of from about 50 to 50,000 for example, mixtures of polyethers and polyesters.

Low molecular weight compounds containing at least two reactive hydroxyl groups (molecular weight from about 50 to 400) suitable for use in accordance with the present invention are compounds preferably containing hydroxyl groups and
15 generally containing from about 2 to 8, preferably from about 2 to 4 reactive hydroxyl groups. It is also possible to use mixtures of different compounds containing at least two hydroxyl groups and having a molecular weight in the range of from about 50 to 400. Examples of such compounds are ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol, 1,5-pentanediol,
20 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 1,4-cyclohexane dimethanol, 1,4-cyclohexanediol, trimethylolpropane, 1,4-bis-hydroxymethyl cyclohexane, 2-methyl-1,3-propanediol, dibromobutenediol (U.S. Patent No. 3,723,392), glycerol, trimethylolpropane, 1,2,6-hexanetriol, trimethylolethane, pentaerythritol, quinitol, mannitol, sorbitol, diethylene glycol, triethylene glycol, tetraethylene
25 glycol, higher polyethylene glycols, dipropylene glycol, higher polypropylene glycols, dibutylene glycol, higher polybutylene glycols, 4,4'-dihydroxy diphenyl propane and dihydroxy methyl hydroquinone.

Other polyols suitable for the purposes of the present invention are the mixtures of hydroxy aldehydes and hydroxy ketones ("formose") or the polyhydric
30 alcohols obtained therefrom by reduction ("formitol") which are formed in the autocondensation of formaldehyde hydrate in the presence of metal compounds as

catalysts and compounds capable of enediol formation as co-catalysts (see, for example, German Offenlegungsschrift Nos. 2,639,084, 2,714,084, 2,714,104, 2,721,186, 2,738,154 and 2,738,512).

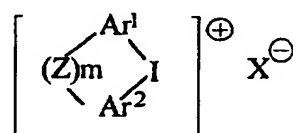
It is contemplated that polyfunctional alcohols such as carbowaxes,
5 poly(ethylene glycol), poly(ethylene glycol methyl ether), poly(ethylene glycol) tetrahydrofurfuryl ether, poly(propylene glycol) may also be used in the compositions of the present invention.

Mixtures of THV and epoxies within the present invention can define a miscibility window having a composition range that allows for the manufacture of
10 semi-IPNs. No depression in the crystallization onset of THV 200 was observed upon the incorporation of an epoxy monomer. Crystalline point depression in combination with melting point depression was indicative of thermodynamic partial miscibility. Partial miscibility means that only over a narrow range of conditions, that is composition/temperature/pressure, was a homogeneous solution observed.
15 The area of the crystallization exotherms and melting endotherms decreased with increasing epoxy content for the THV/epoxy semi-IPN, as was shown by differential scanning measurements taken between room temperature and 200°C. This demonstrated that the crystalline content of the fluoropolymer, which was relatively low (<20%), was being adversely affected by the presence of the epoxy
20 monomer. It is believed that most of the epoxy monomer was taken up by (swelled) the amorphous component of the THV.

Catalysts for curing the epoxy of the present invention can be activated by either thermal means or photochemical means. Preferred catalysts are thermally activated.

25 Known photocatalysts are of two general types: onium salts and cationic organometallic salts, and both are useful in the invention.

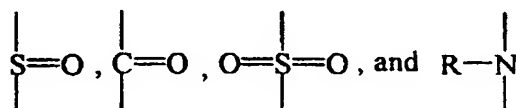
Onium salt photoinitiators for cationic polymerizations include iodonium and sulfonium complex salts. Useful aromatic iodonium complex salts are of the general formula:



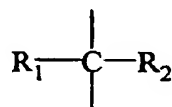
wherein

Ar¹ and Ar² are the same or different and are aromatic groups having from 4 to about 20 carbon atoms, and are selected from the group consisting of phenyl, thienyl, furanyl, and pyrazolyl groups;

Z is selected from the group consisting of oxygen, sulfur, a carbon-carbon bond,



wherein R is an aryl group (having from 6 to about 20 carbon atoms, such as phenyl) or acyl group (having from 2 to about 20 carbon atoms, such as acetyl, or benzoyl), and



wherein R₁ and R₂ are selected from the group consisting of hydrogen, alkyl groups having from 1 to about 4 carbon atoms, and alkenyl groups having from 2 to about 4 carbon atoms;

m is zero or 1; and

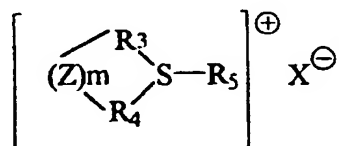
X has the formula DQ_n, wherein D is a metal from Groups IB to VIII or a metalloid from Groups IIIA to VA of the Periodic Chart of the Elements (Chemical Abstracts version), Q is a halogen atom, and n is an integer having a value of from 1 to 6. Preferably, the metals are copper, zinc, titanium, vanadium, chromium, magnesium, manganese, iron, cobalt, or nickel and the metalloids preferably are boron, aluminum, antimony, tin, arsenic and phosphorous. Preferably, the halogen, Q, is chlorine or fluorine. Illustrative of suitable anions are BF₄⁻, PF₆⁻, SbF₆⁻, FeCl₄⁻, SnCl₅⁻, AsF₆⁻, SbF₅OH⁻, SbCl₆⁻, SbF₅⁻², AlF₅⁻², GaCl₄⁻, InF₄⁻, TiF₆⁻², ZrF₆⁻, CF₃SO₃⁻, N(SO₂CF₃)₂⁻, and C(SO₂CF₃)₃⁻. Preferably, the anions are BF₄⁻, PF₆⁻, SbF₆⁻, AsF₆⁻, SbF₅OH⁻, and SbCl₆⁻. More preferably, the anions are SbF₆⁻, AsF₆⁻, and SbF₅OH⁻.

The Ar₁ and Ar₂ aromatic groups may optionally have one or more fused benzo rings (*e.g.*, naphthyl, benzothienyl, dibenzothienyl, benzofuranyl, dibenzofuranyl, etc.). The aromatic groups may also be substituted, if desired, by one or more non-basic groups if they are essentially non-reactive with epoxide and hydroxyl functionalities.

Useful aromatic iodonium complex salts are described more fully in U.S. Patent No. 4,256,828, incorporated herein by reference. The preferred aromatic iodonium complex salts are (Ar)₂I PF₆ and (Ar)₂I SbF₆.

The aromatic iodonium complex salts useful in the invention are photosensitive only in the ultraviolet region of the spectrum. However, they can be sensitized to the near ultraviolet and the visible range of the spectrum by sensitizers for known photolyzable organic halogen compounds. Illustrative sensitizers include aromatic amines and colored aromatic polycyclic hydrocarbons, as described in U.S. Patent No. 4,250,053, incorporated herein by reference.

Aromatic sulfonium complex salt initiators suitable for use in the invention are of the general formula



wherein

R₃, R₄ and R₅ can be the same or different, provided that at least one of the groups is aromatic. These groups can be selected from the group consisting of aromatic groups having from 4 to about 20 carbon atoms (*e.g.*, substituted and unsubstituted phenyl, thienyl, and furanyl) and alkyl groups having from 1 to about 20 carbon atoms. The term "alkyl" includes substituted alkyl groups (*e.g.*, substituents such as halogen, hydroxy, alkoxy, and aryl). Preferably, R₃, R₄ and R₅ are each aromatic; and

Z, m and X are all as defined above with regard to the iodonium complex salts.

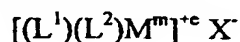
If R₃, R₄ or R₅ is an aromatic group, it may optionally have one or more fused benzo rings (*e.g.*, naphthyl, benzothienyl, dibenzothienyl, benzofuranyl,

dibenzofuranyl, etc.). The aromatic groups may also be substituted, if desired, by one or more non-basic groups if they are essentially non-reactive with epoxide and hydroxyl functionalities.

Triaryl-substituted salts such as triphenylsulfonium hexafluoroantimonate
5 and p-(phenyl(thiophenyl)diphenylsulfonium hexafluoroantimonate are the preferred sulfonium salts. Useful sulfonium salts are described more fully in U.S. Patent No. 5,256,828.

The aromatic sulfonium complex salts useful in the invention are
photosensitive only in the ultraviolet region of the spectrum. However, they can be
10 sensitized to the near ultraviolet and the visible range of the spectrum by a select group of sensitizers such as described in U.S. Patent Nos. 4,256,828 and 4,250,053.

Suitable photoactivatable organometallic complex salts useful in the
invention include those described in U.S. Patent Nos. 5,059,701, 5,191,101, and
5,252,694, each of which is incorporated herein by reference. Such salts of
15 organometallic cations have the general formula:



wherein

M^m represents a metal atom selected from elements of periodic groups IVB,
VB, VIB, VIIB and VIII, preferably Cr, Mo, W, Mn, Re, Fe, and Co;

20 L^1 represents none, one, or two ligands contributing π -electrons that can be the same or different ligand selected from the group consisting of substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing two to twelve π -electrons to the valence shell of the metal
25 atom M. Preferably, L^1 is selected from the group consisting of substituted and unsubstituted η^3 -allyl, η^5 -cyclopentadienyl, η^7 -cycloheptatrienyl compounds, and η^6 -aromatic compounds selected from the group consisting of η^6 -benzene and substituted η^6 -benzene compounds (e.g., xylenes) and compounds having 2 to 4 fused rings, each capable of contributing 3 to 8 π -electrons to the valence shell of
30 M^m ;

L^2 represents none or 1 to 3 ligands contributing an even number of σ -electrons that can be the same or different ligand selected from the group consisting of carbon monoxide, nitrosonium, triphenyl phosphine, triphenyl stibine and derivatives of phosphorous, arsenic and antimony, with the proviso that the total electronic charge contributed to M^m by L^1 and L^2 results in a net residual positive charge of e to the complex; and

e is an integer having a value of 1 or 2, the residual charge of the complex cation;

X is a halogen-containing complex anion, as described above.

Examples of suitable salts of organometallic complex cations useful as photoactivatable catalysts in the present invention include:

- (η^6 -benzene)(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$
- (η^6 -toluene)(η^5 -cyclopentadienyl) $Fe^{+1} AsF_6^-$
- (η^6 -o, p, or m-xylene)(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$
- (η^6 -cumene)(η^5 -cyclopentadienyl) $Fe^{+1} PF_6^-$
- (η^6 -xylenes (mixed isomers))(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$
- (η^6 -xylenes (mixed isomers))(η^5 -cyclopentadienyl) $Fe^{+1} PF_6^-$
- (η^6 -o-xylene)(η^5 -cyclopentadienyl) $Fe^{+1} CF_3SO_3^-$
- (η^6 -m-xylene)(η^5 -cyclopentadienyl) $Fe^{+1} BF_4^-$
- (η^6 -mesitylene)(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$
- (η^6 -hexamethylbenzene)(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$ and
- (η^6 -fluorene)(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$.

Preferred salts of organometallic complex cations useful in the invention include one or more of the following: (η^6 -xylenes (mixed isomers))(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$, (η^6 -xylenes (mixed isomers))(η^5 -cyclopentadienyl) $Fe^{+1} PF_6^-$, (η^6 -o, p, or m-xylene)(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$, and (η^6 -mesitylene)(η^5 -cyclopentadienyl) $Fe^{+1} SbF_6^-$.

Optionally, the organometallic salt initiators can be accompanied by an accelerator such as an oxalate ester of a tertiary alcohol. The accelerator preferably comprises from 0.01 to 10 percent by weight, preferably from 0.1 to 4% by weight of the total polymerizable mixture (thermoplastic component, thermosetting

component and catalyst(s)), as described in U.S. Patent No. 5,252,694, which is incorporated herein by reference.

Useful commercially available initiators include FX-512, an aromatic sulfonium complex salt (3M Company, St. Paul, MN), UVITM-6974, an aromatic sulfonium complex salt (Union Carbide Corp., Danbury, CT) and IRGACURETM 261, a cationic organometallic complex salt (Ciba Geigy Chemicals, Hawthorne, NY).

Photoinitiators useful in the invention can be present in an amount in the range of 0.01 to 10 weight percent, preferably 0.1 to 5, and most preferably 0.1 to 2 weight percent based on total curable resin composition.

Certain thermally-activated curing agents for epoxy resins (*e.g.*, compounds that effect curing and crosslinking of the epoxide by entering into a chemical reaction therewith) are useful in the present invention. Preferably, such curing agents are thermally stable at temperatures at which mixing of the components takes place.

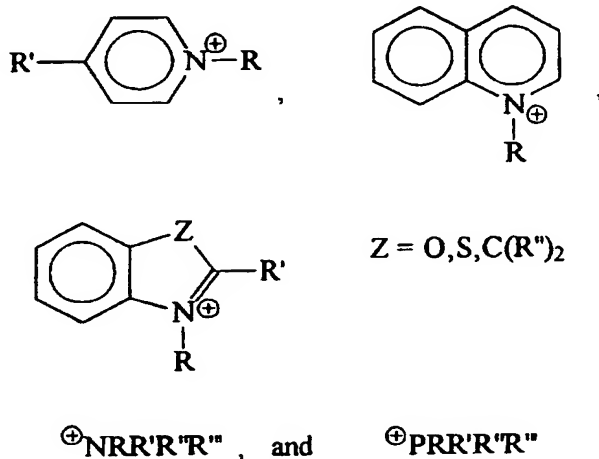
Suitable thermal curing agents include aliphatic and aromatic primary and secondary amines, *e.g.*, di(4-aminophenyl)sulfone, di(4-aminophenyl)ether, and 2,2-bis-(4-aminophenyl)propane; aliphatic and aromatic tertiary amines, *e.g.*, dimethylaminopropylamine and pyridine; quaternary ammonium salts, particularly pyridinium salts such as N-methyl-4-picolinium hexafluorophosphate; fluorene diamines, such as those described in U.S. Patent No. 4,684,678, incorporated herein by reference; boron trifluoride complexes such as $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and $\text{BF}_3 \cdot \text{H}_2\text{NC}_2\text{H}_5\text{OH}$; imidazoles, such as methylimidazole; hydrazines, such as adipohydrazine; and guanidines, such as tetramethylguanidine and dicyandiamide (cyanoguanidine, commonly known as DiCy). It is to be understood that a careful choice among these curing agents must be made, since many of them would be unsuitable for use when high-melting polyolefin components are present, but that they may be useful in preparing semi-IPNs of the invention that comprise low-melting polyolefins and epoxy resins.

High temperature epoxy catalysts are particularly useful in the present invention. It has been found that simple pyridinium, quinolinium, indoleninium,

benzothiazolium, alkyl, aryl and alkylaryl ammonium and phosphonium salts are effective initiators of the cationic polymerization of epoxies in the 250 to 350°C range. Because of these high exotherm temperatures, these catalysts are particularly suited to use with the higher extrusion temperatures of, for example, fluoroelastomers, of 200°C or greater. The compositions are stable in the extruder, i.e., they do not cure, eliminating problems that would be caused by crosslinking during this processing step. When finally cured, these compositions give surprisingly high overlap shear bond strengths.

In general, cationic nitrogen centered salts are active in this temperature range. A surprising result is the order of the exotherm temperatures for a series of these compounds when the anion is varied and the cation is held constant. The exotherm temperatures increase in the order $\text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$. This is surprising in that those skilled in the epoxy resin art would expect the order to be the reverse.

Classes of salts useful as thermal curatives include pyridinium, quinolinium, benzoxazolium, benzothiazolium, indolenium, ammonium, and phosphonium salts. Structures of salts that have been found to be particularly suitable as catalysts in the epoxy/polypropylene compositions include:



20

wherein R is an alkyl group or an aryl group, R' is an alkyl group or an acyl group or an aryl group, R'' is an alkyl group or an aryl group, R''' is an alkyl group or an aryl group. R and R' together can form a ring structure of from 4 to 8 carbon

atoms. (R, R' and R'' together can form a bicyclic ring structure.) Alkyl groups can have 1 to 12 carbon atoms, and aryl groups can be 1 to 3 fused rings (e.g., naphthalene) or joined rings (e.g., biphenyl) having up to 30 carbon atoms. Each cationic charge must be balanced by the appropriate number of anions, X⁻.

5 and wherein X⁻ can be as previously defined, preferably X⁻ is BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, or CF₃SO₃⁻, and most preferably, X⁻ is PF₆⁻.

 wherein each R, R', R'', R''' independently can be an alkyl, aryl, or alkaryl group having up to 20 carbon atoms, and X is as previously defined.

 Thermal curatives can be present in an amount such that the ratio of epoxy
10 equivalents to thermal epoxy curative equivalents is in the range of 0.9:1 to 2:1.

 Photocuring can take place before the thermoplastic crystallizes or after crystallization takes place. For most potential uses, curing of the film is not required until it is ready to be made into the final product. Curing in-line can be desirable when molecular orientation of the thermoplastic needs to be preserved.

15 Various adjuvants can also be added to the compositions of the invention to alter the physical characteristics of the cured semi-IPN. Included among useful adjuvants are thixotropic agents such as fumed silica; pigments to enhance color tones such as ferric oxide, carbon black and titanium dioxide; fillers such as mica, silica, acicular wollastonite, calcium carbonate, magnesium sulfate and calcium
20 sulfate; clays such as bentonite; glass beads and bubbles; reinforcing materials such as unidirectional woven and nonwoven webs of organic and inorganic fibers such as polyester, polyimide, glass fibers, polyamides such as poly(p-phenylene terephthalamide), carbon fibers, and ceramic fibers. Amounts up to about 200 parts of adjuvant per 100 parts of polyolefin-epoxy composition can be used.

25 In addition to the above-mentioned additives and adjuvants, it is within the scope of the invention to include one or both of polyolefins and polyamides in admixture with the fluoropolymer resins and epoxy resins.

 As used herein, "polyolefins" preferably refers to fully pre-polymerized polymeric hydrocarbons bearing essentially no organic functional groups, prepared
30 from homopolymerization and/or copolymerization of hydrocarbon olefinic monomers by cationic-, anionic-, or Ziegler-Natta-type polymerization processes.

Homopolymeric polyolefins useful in the invention include polyethylene, polypropylene, poly-1-butene, poly-1-pentene, poly-1-hexene, poly-1-octene and related polyolefins. Preferred homopolymeric polyolefins include polyethylene (e.g., Dow 25455™, available from Dow Chemical Co., Midland, MI) and
5 polypropylene (e.g., Shell DS5D45™, available from Shell Chemicals, Houston, TX, or Exxon 3445™ and 3505™, available from Exxon Chemicals, Houston, TX). Also useful are copolymers of these alpha-olefins, including poly(ethylene-co-propylene) (e.g., SRD7-462™, SRD7-463™ and DS7C50™, each of which is available from Shell Chemicals), poly(propylene-co-1-butene) (e.g., SRD6-328™,
10 also available from Shell Chemicals), and related copolymers. Preferred copolymers are poly(ethylene-co-propylene). Also useful is the Vestoplast™ series of polyolefins, available from Hüls America Inc., Piscataway, NJ.

Polyolefins useful in the invention can be present in an amount such that the ratio of fluoropolymer to polyolefin is within the range of 1:99 to 99:1, preferably
15 25:75 to 75:25, and most preferably 50:50. When mixtures of polyolefins and fluoropolymers are present, the epoxy resin component preferably comprises from about 10 to about 15 % by weight of the total weight of the mixture, for all ratios of polyolefin:fluoropolymer.

As used herein, "polyamides" refers to fully pre-polymerized condensation
20 polymers characterized by the presence of the amide group, -CONH-, in the polymer backbone. Polyamides are prepared, e.g., by the condensation polymerization of a polyfunctional carboxyl-containing species such as a dicarboxylic acid or a dicarboxylic acid halide with a polyfunctional amine, or by self-condensation of a bifunctional molecule that has both amine- and carboxyl-
25 functionality. The reactive species can be individually aliphatic, aromatic, carbocyclic, polycyclic, saturated, unsaturated, straight chain or branched. Polyamides can be the polymerization product of a single polycarboxyl-functional species with a single polyamine species as well as the polymerization product of a mixture of polycarboxyl species and a mixture of polyamine species. Industry has
30 developed a number of routes to polyamides, all of which are intended to be included in the present definition. While the general class of polyamides known as

"nylon" is the most abundant in commerce, the present definition is not intended to be limited thereto. Preferred polyamides for the present invention include Nylon 6, Nylon 66, Nylon 12, and the family of Nylon materials available from DuPont Co., Wilmington, DE and the Versamide™ family of polyamides available from Henkel Corp., Ambler, PA..

Polyamides useful in the invention can be present in an amount such that the ratio of fluoropolymer to polyamide is within the range of 1:99 to 99:1, preferably 25:75 to 75:25, and most preferably 50:50. When mixtures of polyamides and fluoropolymers are present, the epoxy resin component preferably comprises from about 10 to about 15 % by weight of the total weight of the mixture, for all ratios of polyamide:fluoropolymer.

The fluoropolymer-epoxy semi-IPNs are useful as protective coatings, adhesives, self-supported films, and in multilayer assemblies. More particularly, the semi-IPNs of the invention are useful as structural adhesives for metals, plastics, glass or ceramics; as free-standing hot melt adhesives; or as protective coatings. In a preferred embodiment, the fluoropolymer-epoxy semi-IPN can be coated on a flexible substrate to produce an adhesive tape. In specialty applications, the semi-IPN coatings and films can be in multilayer assemblies for electrical and communication cables. In an additional preferred embodiment, the fluoropolymer-epoxy semi-IPN can be coated on a polymeric, preferably polyolefin, more preferably polypropylene, tank or vessel used for storage or transporting hydrocarbon fuels such as gasoline, wherein the semi-IPN of the invention can be an intermediate (or "tie") coating that acts as a binding agent between the polyolefin vessel and a subsequent fluoropolymer (*e.g.*, poly(tetrafluoroethylene) (PTFE)) protective coating. Semi-IPNs of the invention also find use directly as interior coatings for metal tanks or vessels used for transportation and storage of corrosive chemicals.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

EXAMPLES

Test Procedures

Tensile Modulus, Tensile Strength

- 5 Tensile modulus and tensile strength were measured using an Instron tensile testing machine (Instron Corp., Park Ridge, IL), model 1122, equipped with a 5KN load cell, model 2511-317. Cross-head speeds and gauge lengths varied for each test, as indicated.

10 Overlap Shear, Peak Load

- Overlap Shear measurements were obtained essentially according to ASTM D1002-94, "Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading." Cold rolled steel coupons measuring 11.43 cm x 2.54 cm x 3.2 mm were thoroughly cleaned with methyl ethyl ketone and heated on
- 15 a hot plate to temperatures of from about 185 to about 250°C. Films having thicknesses of from about 0.25 and 0.75 mm were applied to the hot metal surface using a silicon rubber roller and allowed to melt. Films containing photocatalysts were exposed, while molten, to 3.1 J/cm² of radiant energy from TLD 15W/03 (Phillips, Holland) or 350BL (Siemens Corp./Osram Sylvania Inc. Danvers, MA)
- 20 UV-emitting lamps. The two cured halves were joined together, film side-to-film side, by means of Scotchkote™ 134 Epoxy (3M, St. Paul, MN). The area of overlap was 2.54 cm². A very thin layer of Scotchkote™ 134 was dusted on to one half and the other half placed atop it at 185°C. Samples containing thermal curing systems were made by placing a piece of the film to be tested between two coupons
- 25 at 225°C for five minutes. Samples were then removed from the heat, cooled to 22°C. Peak loads and strain to break were recorded from an Instron machine with a 44.5 KN load cell.

Dielectric Constant

- 30 Dielectric constant measurements were taken essentially according to ASTM D257-93, using Keithly 237 and 8008 resistivity fixtures and a 60-second

electrification time at 500 volts and 45% relative humidity. 500 mHz measurements were taken with an HP4284A Precision LCR meter equipped with an HP16451B Dielectric Test Fixture (Hewlett-Packard Co., Palo Alto, CA). 900 mHz measurements were taken with an HP4291A Impedance/Material Analyzer, using
5 an HP 16451A Dielectric Test Fixture.

Example 1

Compositions can be prepared in at least two ways. In method A, dried, dehydrofluorinated THV 200™ powder was mixed in a preheated Brabender
10 internal mixer equipped with sigma blades at 185°C with from 2 to 10% by weight of PR500™ based upon the total weight of the thermoplastic polymer component. The samples were then melt pressed to the desired thickness. For additional details of dehydrofluorination see U.S. patent numbers 3,507,844, 4,758,618, and
copending U.S. patent application Serial No. 08/703,422.

15 In method B, a twin screw extrusion machine was used to make the films. PR500™ (comprising mixture of epoxies plus fluorene amine curative) was added by means of a side port downstream from the fluoropolymer pellet feeding port. Samples were extruded at a screw speed of 90 rpm in a Haake counter-rotating conical twin screw extruder (31.8/20 mm (rear/front)) equipped with a static mixer
20 and a 15.2 cm (6") sheet die. The temperature profile from feed to die was (°C): 86-92-92-86. The take up wheel was maintained at 25°C. The line speed was 30.5 cm/min (1 ft/min.), and extrudate thickness was 381 micrometers (15 mil.).

Static and adhesive properties.

25 In semi-IPNs the physical state of the thermoplastic during cure of the thermoset was important to develop a specific set of properties.

Lamination or adhesion on metals was accomplished using UV or thermal cure. For adhesion to take place the substrate needed to be heated above the melting point of the thermoplastic and then irradiated. The minimum cycle for
30 thermally cured systems was 5 minutes at 225°C. Sylvania 350 BL bulbs (Siemens Corp./Osram Sylvania Inc., Danvers, MA), could be used if placed 2.54 cm (1")

above the sample for 5 minutes. After room temperature exposure a subsequent high-temperature oven cure was needed to increase the glass transition temperature, preferably to 150°C or higher in the thermoset phase. Fusion lamps could be used also as long as the radiation dosage was between 2-3 J/cm². The sample was then removed from the heat source and cooled to room temperature. Overlap shear tests were used to quantify adhesion at room temperature. Data of Table 1 show the adhesive properties obtained when the thermoplastic was molten during cure of the thermoset.

**Table 1. Adhesive and mechanical property data
of cured THV200/epoxy semi-IPNs**

Material	Tensile Modulus (MPa)	Tensile Strength (MPa)	Overlap Shear Strength (MPa)
THV, no epoxy	35.5 ± 4.4	15.5 ± 5.2	none
THV+ 4% Epon 828	39.3 ± 6.2	19.6 ± 6.5	4.9 ± 0.5
THV + 4.6% PR500	48.3 ± 5.5	17.4 ± 1.5	5.2 ± 0.3
THV + 4.6% PR500 + 6% G3003	52.4 ± 7.6	17.4 ± 2.8	5.6 ± 0.6
THV + 9.2% PR500 + 5.7% G3003	46.5 ± 0.2	13.1 ± 1.6	4.9 ± 1.3
THV200/DS7C50(1/1)	360.8 ± 35.4	18.6 ± 0.6	none
THV200/DS7C50(1/1) + 5.7% G3003	475.9 ± 58.8	19.9 ± 0.7	none
THV200/DS7C50(1/1) + 9.2%PR500+5.7% G3003	355.2 ± 29.0	16.2 ± 1.1	11.3 ± 1.6
THV(0.66 mole percent dehydrofluorinated latex) + 5% PR500	--	--	11.6 ± 1.2
THV(3.0 mole percent dehydrofluorinated latex) + 10% PR500	--	--	3.6 ± 0.5

Epon™ 828 = aromatic epoxy (Shell Chemicals, Houston, TX) (photo curing system)
 PR500™ = mixture of epoxies + fluorene diamine curative (3M Co., St. Paul, MN) (thermal curing system)
 G3003 (Epolene™ G 3003) = maleated polypropylene wax (Eastman Chemical Co., Kingsport, TN)
 DS7C50™ = nonfunctionalized fully saturated stereoregular polyolefin (Shell Chemicals, Houston, TX)

Data in Table 1 show the increase in modulus realized with different compositions. The tensile properties listed are those obtained by curing with fusion lamps at room temperature, that is, curing when the thermoplastic was in the solid state. Low adhesion developed if the thermoplastic was not molten during cure of the thermoset. Increases in tensile modulus were observed when cure took place after the thermoplastic crystallized.

Both UV and thermal cure provided similar overlap shear strength values in the absence of dehydrofluorination. Dehydrofluorination increased the overlap shear strength to about 11.6 MPa. A similar level of adhesion was obtained for the THV/stereoregular-polyolefin/epoxy system. THV/epoxy semi-IPN samples failed adhesively, including those that were dehydrofluorinated. THV/polyolefin/epoxy and polyolefin/epoxy semi-IPNs failed cohesively.

Tensile stiffness increased also with the addition of stereoregular polyolefins to THV/epoxy systems. It is believed this was a very phase separated microstructure. Elongation decreased as a result of the hard inclusions within the soft matrix. The THV/polyolefin/epoxy extrudates had a very good appearance and were easy to extrude. DS7C50 was a polypropylene with a rubbery phase content of 20%. The rubbery phase was a fully saturated ethylene(55%)/propylene copolymer(45%) The molecular weight ratio of rubber to polypropylene homopolymer was 1.5. This rubber content in polypropylene provided optimum adhesive properties in THV/polyolefin/epoxy semi-IPNs.

Example 2

Uses for THV semi-IPN coatings and films can be in multilayer assemblies for electrical and communication cables.

In electrical assemblies, properties such as dielectric strength, dielectric constant, and dielectric loss can be used to determine the usefulness of semi-IPNs of the invention. Results of these measurements for the cured THV 200/epoxy semi-IPNs noted previously are shown in Table 2.

30

Table 2. Dielectric Properties of Cured THV 200/Epoxy Semi-IPNs

Sample	EPONTM 828, wt. %	PR500TM wt. %	Epolene G3003TM wt. %	Shell DS7C50TM wt. %	Dielectric Strength ¹ , kV/25 microns	Dielectric Constant ^{2,3}	Dielectric Loss (tan δ) ^{2,3}
2A (comp.)	0	0	0	0	0.81±0.04	control	control
2B	4	0	0	0	0.80±0.06	lower	lower
2C	0	4.6	0	0	0.63±0.07	same	same
2D	0	4.6	6	0	1.39±0.26	sl. higher	higher
2E	0	9.2	5.7	0	0.86±0.05	same	same
2F	0	9.2	5.7	50	1.72±0.20	much lower	much lower

¹Measured according to ASTM D149-94²Measured according to ASTM D257-93 over a frequency range of 0-200 mHz³Values for Samples B-F are reported relative to Comparative Example A

The data of Table 2 show that mixing a polyolefin (DS7C50) or a maleated polyolefin (Epolene™ G3003) at less than 10 weight percent significantly increases the dielectric strength of THV 200 without affecting the dielectric constant or dielectric loss. At the relatively high loading of 50% by weight of DS7C50 polyolefin, dielectric strength is again significantly increased while both dielectric constant and dielectric loss are significantly decreased. As a comparison, the best short term dielectric strengths for an unoriented plastic evaluated using ASTM D149-94 have been observed in crosslinked polyvinylchloride to be 1.5 kV/25.4 micrometers. It is also noted that addition of a relatively small amount of cationically cured aromatic epoxy (Sample 2B) noticeably decreased both dielectric constant and dielectric loss without affecting dielectric strength of THV 200.

15 Example 3

Epoxy-fluoropolymer semi-IPNs of the invention were prepared by extrusion. Fluoropolymer, epoxy resin, and catalyst were mixed in a Haake conical twin screw extruder (rear diameter: 31.8 mm; front diameter: 20 mm) equipped with Zenith HPB gear pumps having a capacity of 0.16 mL/turn for pumping monomer into the extruder. Temperature setpoints in the extruder typically were all set at 271° C, and actual zone temperatures typically were 234 - 273 - 271 - 271°C. Six samples were prepared:

Table 3a. Formulations

Sample	Fluoropolymer	Epoxy	Catalyst
3A (comparative)	FEP-100	none	none
3B	FEP-100	5% Epon 828	MP
3C (comparative)	EP-610	none	none
3D	EP-610	5% Epon 828	MP
3E (comparative)	Kynar 740	none	none
3F	Kynar 740	5% Epon 828	MP

In Table 3a, above, FEP-100 was poly(tetrafluoroethylene-co-hexafluoropropylene), available from Dupont Chemical Co., Wilmington, DE; EP-610 was poly(ethylene-co-tetrafluoroethylene), available from Daikin, Japan; Kynar 740 was poly(vinylidene fluoride), available from Elf Atochem, Philadelphia, PA, and MP was N-methyl-4-picolinium hexafluorophosphate (prepared as in Example 6).

Samples of approximately 380 micrometers thickness were tested qualitatively for adhesion to steel, polyimide film, and Teflon™ film substrates by placing the extrudate (10.16 cm x 2.54 cm) on the substrate and heating the construction to 271° for 5 minutes. Samples 3D and 3F showed limited adhesion to steel, but none to polyimide or Teflon. Samples 3A, 3B, 3C, and 3E showed no adhesion to any substrates under these conditions.

Similarly, a second set of samples was applied to each of the substrates and heated at 271°C for 15 minutes. Again, Samples 3D and 3F showed adhesion to steel. Sample 3B showed slightly greater adhesion to Teflon than to steel, but all other samples showed no adhesion to Teflon. Samples 3D and 3F showed some adhesion to polyimide film.

Adhesion of Sample 3D to steel was further shown as follows. Five strips of Sample 3D, measuring 15 x 2.54 x 0.03 cm, were placed on steel bars measuring 11.4 x 2.54 x 0.03 cm and heated to 299° C for 15 minutes. On cooling, peel values were obtained by placing the steel bar in one clamp of an Instron instrument and excess sample film in the other clamp to measure the 180° peel test. A gauge length of 7.62 cm was used, and crosshead speed was 5.08 cm/min. Data are shown in Table 3b below.

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Table 3b. Sample 3D 180 ° Peel Test (Steel)

Sample	Average Peel (MPa)	Max Peel (MPa)
3D1	0.016	
3D2	0.020	0.029
3D3	0.016	0.024
3D4	0.017	0.042
3D5	0.013	0.013
Average	0.016	0.027
St. Dev.	0.003	0.012

- Tensile properties of Samples 3A-F were obtained, as shown in Table 4 .
- Each formulation was examined in both the "uncured" state, as received directly
- 5 from the extruder, and "cured" by heating the sample at 271°C for 5 minutes. The values reported in Table 4 were obtained at ambient temperature (approximately 23°C); gauge length was 2.54 cm and crosshead speed was 5.08 cm/min. Values are reported based on five samples per datum recorded.

10

Table 4. Tensile Data

Sample	Stress @ Yield (MPa)	% Strain (%)	Modulus (MPa)	Stress @ Max Load (MPa)	Max Load (kg)
3A (comparative)					
Average	13.6	743	320	22.1	24.13
St. Dev.	0.43	44	37.2	1.53	1.69
3A cured (comparative)					
Average	14.58	441	296.6	17.3	15.38
St. Dev.	1.35	224	11.96	2.98	2.18
3B					
Average	12.05	345	309	13.8	9.25
St. Dev.	1.43	217	55.1	2.13	1.91
3B cured					
Average	14.58	138	306.6	14.9	11.1

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Sample	Stress @ Yield	% Strain	Modulus	Stress @ Max Load	Max Load
	(MPa)	(%)	(MPa)	(MPa)	(kg)
St. Dev.	14.50	4.6	62.6	14.5	6.6
3F cured					
Average	36.65	42	932	36.6	20.6
St. Dev.	18.23	22	115	18.2	10.2

The data of Table 4 show that tensile properties of fluoropolymers are not adversely affected by admixture with an epoxy resin and curing agent.

5 Example 4

A semi-IPN construction comprising THV 200 and an 3.4% by weight ERL-4221 epoxy resin (Shell Chemical Co., Houston, TX) was prepared in an extruder with a temperature profile of 192 - 222 - 221 - 219° C and a pellet feed rate of 14.2 g/min. The cast wheel was kept at 20° C; line speed setting was 25.

- 10 Triarylsulfonium hexafluorophosphate (FX-512 Activated Epoxy Curative, 3M Company, St. Paul, MN) catalyst concentration was 1% by weight.

- One portion of the resulting extruded film, measuring 10.2 cm x 2.54 cm x 0.0254 cm, was placed between two pieces of poly(ethylene terephthalate) (PET) release liner (Scotchpar™ polyester film 3M, St. Paul, MN). A second portion, 15 having the same dimensions, was placed between two pieces of PET release liner that had previously been treated with UV light irradiation as described in U.S. Patent No. 4,822,451, Example 5. The two samples were placed on a hot plate at 190° C and irradiated with a Sylvania 350 Blacklight UV generating bulb (Siemens Corp./Osram Sylvania Inc. Danvers, MA) at a distance of 1 cm for 5 minutes. The 20 irradiated samples were cooled and cut into strips measuring 1.27 cm x 10.2 cm, then tested for adhesion to the liners using an Instron tensile testing machine (Model 1122) at a crosshead speed of 1.27 cm/min and a gauge length of 2.54 cm.

Minimum load for untreated PET liner: 0.0092 MPa

Minimum load for UV treated PET liner: 0.0070 MPa

The data show that epoxy-fluoropolymer semi-IPNS of the invention are capable of modest adhesion even to a release liner commonly used in industry.

5 Example 5

Semi-IPNS of the invention comprising blends of THV 500 fluoropolymer and compatible polymers were prepared in a twin-screw extruder as described above. Composition of the blends is shown in Table 5.

10

Table 5. THV Blend Semi-IPNS

Ex.	Blended Polymer	%Blended Polymer	Epoxy Resin	% Epoxy Resin	Catalyst
5A	Versamid(b)	50 (volume)	ERL-4221	6.6	S(a)
5B	Bynel PEAH(c)	50 (volume)	ERL-4221	6.5	S(a)
5C	Bynel SB602(d)	33 (weight)	*	*	none
5D	Versamid(b)	50	ERL-4221	3.3	S(a)
5E	none	none	ERL-4221	3.4	S(a)

(a) Catalyst S = triarylsulfonium hexafluorophosphate (FX-512 Activated Epoxy Curative, 3M Company, St. Paul, MN)

(b) Versamid™ is a nylon resin available by Henkel Corp., Ambler, PA

15 (c) Bynel PEAH™ is an acid-functionalized polyethylene available from Dupont

(d) Bynel XB602™ is an epoxidized polypropylene available from Dupont

* no additional epoxy compound was added

20 Examples 5A - 5E were heated at 185° C on a Teflon-covered hot plate under UV irradiation (Sylvania Blacklight bulbs) at a distance of 1cm for 5 minutes while in contact with the following polymer films:

1. PET release liner (Scotchpar™ polyester film)
2. Polyolefin 1150-1™ (Eastman Chemicals, Kingsport, TN)
3. Elvamide™ 8064 Nylon film (Dupont Chemical Co., Wilmington, DE)
- 25 4. 5 % Epolene™ (C18) wax (Eastman Chemicals) in Tenite™ 1550P polyethylene (Eastman Chemical Co.)

5. Exxact 4038TM polyolefin, metallocene catalyst (Exxon Chemicals, Houston, TX)

6. Exxon 3445TM propylene homopolymer (Exxon Chemicals) mixed with 25% ERL-4221TM Epoxy resin (Union Carbide).

5

Adhesion of epoxy-polymer blend semi-IPNS of this Example to the six films was qualitatively observed, as follows:

Examples 5A - 5E showed adhesion to PET (Film 1) and Nylon (Film 3):

Example 5B also showed adhesion to wax-filled polyethylene (TeniteTM 1550P) (Film 4) and metallocene polyolefin (Film 5);

Example 5C also showed adhesion to polyolefin 1150-1 (Film 2), metallocene polyolefin (Film 5) and polypropylene-epoxy (Film 6).

Data of Example 5 show that cured blends of nylon or functionalized polyolefins with THV-Epoxy semi-IPNS of the invention exhibited good adhesion to a number of polymeric substrates. The blends can be useful as tie layers in multi-layer polymeric constructions to help adhere a protective coating to a polymeric substrate such as polyethylene.

20 Example 6

N-Methyl-4-picolinium hexafluorophosphate catalyst (Catalyst MP) was prepared as follows:

A solution of 50 g 4-picoline (Aldrich Chemicals) and 76.2 g iodomethane (Aldrich Chemicals) in 600 mL 1,2-dichloromethane was stirred at room temperature, approximately 23° C. After a mild reaction exotherm, a precipitate formed, and the mixture was stirred for approximately 3 hours as it cooled to room temperature. The solid product was collected by filtration, washed with 2 x 250 mL 1,2-dichloromethane, 2 x 250 mL petroleum ether, air dried, then dried in an oven under vacuum at 50° C overnight. An off-white solid, N-methyl-4-picolinium iodide (106 g) was obtained.

A solution of 35 g N-methyl-4-picolinium iodide in 200 mL water was treated with 24.3 g ammonium hexafluorophosphate (Aldrich Chemicals) that had been previously dissolved in a minimum amount of water. A precipitate formed as the two solutions were mixed. The precipitate was collected on a filter, washed
5 with 2 x 100 mL water, dried on the funnel, then dried overnight in a vacuum oven at 50° C. A total of 30 g of white, solid N-methyl-4-picolinium hexafluorophosphate was obtained, mp. 210° by Differential Scanning Calorimetry (DSC). Identity of the product was confirmed by IR and NMR spectroscopy.

Various modifications and alterations of this invention will become apparent
10 to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

CLAIMS:

1. A curable composition comprising:
 - a) more than zero to 75 weight percent epoxy resin,
 - 5 b) an effective amount of a curative for the curable epoxy resin, and optionally one or both of a sensitizer and an accelerator for the curative,
 - c) 25 to less than 100 weight percent of a fully prepolymerized uncrosslinked fluoropolymer, based on the weight of the total epoxy-fluoropolymer composition, and
 - 10 d) optionally, one or both of a polyolefin and a polyamide.
2. The composition according to claim 1 wherein said fluoropolymer is selected from the group consisting of poly(tetrafluoroethylene), poly(tetrafluoroethylene-co-hexafluoropropylene), poly(ethylene-co-
15 tetrafluoroethylene), poly(ethylene-co-tetrafluoroethylene-co-hexafluoropropylene), poly(vinylidene fluoride), poly(chlorotrifluoroethylene), and a terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride (THV).
3. The composition according to claims 1 or 2 wherein said
20 fluoropolymer comprises in the range of 0.01 to 20 mole percent dehydrofluorinated fluoropolymer.
4. The composition according to any of claims 1 to 3 wherein said epoxy resin comprises one or more 1,2-, 1,3-, and 1,4-cyclic ethers.
25
5. The composition according to any of claims 1 to 4 wherein said curative is selected from the group consisting of photo curatives and thermal curatives activated at temperature of 170° C or higher.
- 30 6. The composition according to claim 5 wherein said photocurative is selected from the group consisting of iodonium and sulfonium complex salts and

organometallic complex salts and said thermal curative is selected from the group consisting of aliphatic and aromatic primary and secondary amines, aliphatic and aromatic tertiary amines, quaternary ammonium salts, fluorene diamines, boron trifluoride complexes, hydrazines, guanidines, and salts of pyridinium, quinolinium, benzoxazolium, benzothiazolium, indolenium, ammonium, and phosphonium ions.

7. The composition according to any of claims 1 to 6 wherein said epoxy resin is selected from the group consisting of aromatic polyepoxides, aliphatic cyclic polyepoxides, and aliphatic polyepoxides.

10

8. The composition according to any of claims 1 to 7 which is one or more of a hot melt adhesive, a coating on a substrate, and incorporated into an adhesive tape construction.

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9. The cured composition according to any of claims 1 to 8.

10. The cured composition according to claim 9 which comprises a fluoropolymer-epoxy semi-IPN.

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11. The cured composition according to any of claims 1 to 10 which is one or more of a coating on a substrate, a structural adhesive, incorporated into a multilayer assembly, and a self-supporting film or foam.

12. A method for making a semi-interpenetrating polymer according to claim 10 comprising the steps of Methods I or II:

Method I:

a) providing, at a temperature below the thermal activation temperature of the catalyst, a mixture comprising

30

1) a curable epoxy resin,

2) an effective amount of a thermal curative for the curable epoxy resin having an activatable temperature of 170° C or higher, and

3) a fully prepolymerized uncrosslinked fluoropolymer, optionally up to 20 weight percent of which is dehydrofluorinated,

5 4) optionally, at least one of a polyolefin and a polyamide,

b) increasing the temperature above the thermal activation temperature of the catalyst for a time sufficient to effect cure of said epoxy resin; and

Method II:

10 A method for making a semi-interpenetrating polymer according to claim 10 comprising the steps of:

a) providing a mixture comprising

1) a curable epoxy resin,

2) an effective amount of a photoinitiator for the curable epoxy

15 resin, and

3) a fully prepolymerized uncrosslinked fluoropolymer,

4) optionally, at least one of a polyolefin and a polyamide,

b) exposing said mixture to UV radiation for a time sufficient to effect cure of said epoxy resin.

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INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 97/13561

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D163/00 C09J163/00 C08L63/00 C08L27/12 //(C08L63/00,
27:12),(C08L27/12,63:00),(C08L63/00,27:12,23:00),(C08L63/00,
27:12,77:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 169 187 A (GLAZAR, BARBARA L.) 25 September 1979	1,2,4-12
Y	see abstract; example 3 see column 5, line 17 - column 6, line 22 ---	3
Y	EP 0 204 943 A (AGRU ALOIS GRUBER & SOHN OHG) 17 December 1986 see column 2, line 34 - line 55 ---	3
X	EP 0 084 771 A (ALLIED CORP.) 3 August 1983 see claims 1,2,8,9; examples 1,3 see page 4, line 27 - page 5, line 9 see page 7, line 8 - page 8, line 4 --- -/--	1,2,4-12

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- "S" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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PCT/US 97/13561

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	<p>EP 0 292 203 A (STANDARD OIL CO.) 23 November 1988 see claims 1-9 see page 5, line 9 - page 6, line 48</p>	1,2,4-7, 9,10,12
X	<p>DE 15 19 010 A (ACHESON IND.) 13 November 1969 see claims 1-7; example 1</p>	1,2,4, 7-11
X	<p>DATABASE WPI Week 9334 Derwent Publications Ltd., London, GB; AN 93-269987 XP002048384 & JP 05 186 757 A (DAINIPPON INK & CHEM. KK; IGETA KOHAN KK; SUMITOMO METAL IND. INC.) , 27 July 1993 see abstract</p>	1,2,4, 7-11
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A	<p>MASCIA L ET AL: "MECHANICAL PROPERTIES AND THERMAL AGEING OF A PERFLUOROETHER- MODIFIED EPOXY RESIN IN CASTINGS AND GLASS FIBRE COMPOSITES" COMPOSITES, vol. 26, no. 5, 1 May 1995, pages 379-385, XP000508199 see page 379 - page 380</p>	10,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/13561

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